PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 08 May 2000 (08.05.00)	
International application No. PCT/AU99/00791	**Applicant's or agent's file reference** C99090
International filing date (day/month/year) 17 September 1999 (17.09.99)	**Priority date** (day/month/year) 18 September 1998 (18.09.98)
Applicant TORPY, Keith, Mario et al	

1. The designated Office is hereby notified of its election made:

   ☒ in the demand filed with the International Preliminary Examining Authority on:

   04 April 2000 (04.04.00)

   ☐ in a notice effecting later election filed with the International Bureau on:

   ____

2. The election ☒ was ☐ was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Juan Cruz Telephone No.: (41-22) 338.83.38

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00791

A.	CLASSIFICATION OF SUBJECT MATTER
Int. Cl. 7:	A61K 007/38; A45D 034/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: A61K, SEARCH TERMS AS BELOW

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC AS ABOVE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT: (A61K 007/ic OR A45D 034/ic) AND solid AND (alum: OR alum:()sulfate OR alum:()sulphate OR alum:()chlorohydrate OR alum:()chlorohydroxide) AND (spray OR pump)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	US 5,997,850 A (Xiaozhong Tang et al.) 7 December 1999 See whole document	All claims
P,A	US 5,976,514 A (Gerald John Guskey, et al.) 2 November 1999 See whole document	All claims
A	AU-A-34153/97 (693744) (Techville Pty. Ltd.) 2 July 1998 See whole document	All claims

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 November 2000	14 NOV 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer MICHAEL GRIEVE Telephone No : (02) 6283 2267

Box I Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos :

   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos : **all claims**

   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

   The "claims" as presently drafted are extremely broad and ill defined, and hence were very difficult to search for ISR puropses.

   As a result, the following inventive concept (as determined by the IS examiner) was searched:

   solid alum salt-based products in a liquid dispensing container, and the use of such products as deodorants

3. ☐ Claims Nos :

   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/00791

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	5997850	AU	13638/99	BR	9813320	EP	1027031
		NO	20002232	WO	9921528	US	6066314
US	5976514	AU	62412/99	WO	200030598		
AU	34153/97	NONE					

END OF ANNEX

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

16

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference C99090	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International application No. **PCT/AU99/00791**	International filing date *(day/month/year)* 17 September 1999	Priority Date *(day/month/year)* 18 September 1998

International Patent Classification (IPC) or national classification and IPC

Int. Cl. 7 H05B 3/14

Applicant

EMAIL LIMITED et al

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of **10** sheet(s).

3. This report contains indications relating to the following items:

I	[X]	Basis of the report
II	[ ]	Priority
III	[ ]	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	[ ]	Lack of unity of invention
V	[X]	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	[ ]	Certain documents cited
VII	[ ]	Certain defects in the international application
VIII	[ ]	Certain observations on the international application

Date of submission of the demand 4 April 2000	Date of completion of the report 11 April 2000
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer **Ian Barrett** Telephone No. (02) 6283 2189

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/AU99/00791

I. Basis of the report

1. With regard to the **elements** of the international application:*

   [ ] the international application as originally filed.

   [X] the description, pages , as originally filed,
   pages **1-6,** filed with the demand,
   pages , received on with the letter of

   [X] the claims, pages , as originally filed,
   pages , as amended (together with any statement) under Article 19,
   pages **7-10,** filed with the demand,
   pages , received on with the letter of

   [X] the drawings, pages **1,** as originally filed,
   pages , filed with the demand,
   pages , received on with the letter of

   [ ] the sequence listing part of the description:
   pages , as originally filed
   pages , filed with the demand
   pages , received on with the letter of

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
   These elements were available or furnished to this Authority in the following language which is:

   [ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

   [ ] the language of publication of the international application (under Rule 48.3(b)).

   [ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, was on the basis of the sequence listing:

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readable form.

   [ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

4. [ ] The amendments have resulted in the cancellation of:

   [ ] the description, pages
   [ ] the claims, Nos.
   [ ] the drawings, sheets/fig.

5. [ ] This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report*

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims **1-29**	**YES**
	Claims	**NO**
Inventive step (IS)	Claims **1-29**	**YES**
	Claims	**NO**
Industrial applicability (IA)	Claims **1-29**	**YES**
	Claims	**NO**

2. Citations and explanations (Rule 70.7)

The prior art cited (SU 886328, CN 1082803 & US 4849252) shows that metal oxide heating elements doped with a rare earth element are known. The prior art devices were manufactured by pyrolisis of inorganic compounds. There is nothing to suggest that the film should be deposited from an organometallic base solution, which has advantages over the prior art (see page 1 line 21-24, page 2 lines 4-6 and 13-16).

The heating element of claims 1-18 and the method for manufacturing it in claims 19-29 is novel and inventive as the use of an organometallic base solution has advantages and is not obvious from the prior art.

THIN FILM HEATING ELEMENT

BACKGROUND OF THE INVENTION

This invention relates to heating elements of the kind including an electrically conductive metal oxide film on an electrically insulating substrate.

Such devices are known, and may for example consist of a thin film of tin oxide deposited on a glass substrate by means of pyrolitic deposition.

If such thin film heating elements are to be used in electrical appliances such as cooktops, it is desirable that they be capable of operating at high temperatures, up to 650°C. In applications such as electric kettles where the heating element is small, the element must be capable of handling high power densities, of the order of 10- 20 Watts cm^{-2}. Prior art devices have not proved satisfactory in these conditions. It has been found by the present applicants that tin oxide layers tend to become unstable with increasing temperature, due to the tendency for the oxide to change state. It has also been found that where fluorine is employed as an electron donor or conductivity carrier the properties of the film change irreversibly with increasing temperature, apparently due to the fluorine tending to leave the film at temperatures above 400°C.

We have also found that the tin chloride solutions used in the prior art, for example in the spray pyrolysis process, are not stable in conditions of high humidity due to their hygroscopic properties, and this can lead to lack of uniformity in the oxide films produced.

US Patent No. 4,889,974 of Auding, *et al.* describes thin film elements intended for temperatures beyond 600°C, using oxide films doped at high levels with pairs of compensating foreign atoms. The metal oxide films are doped with, maximally, 10 mol % of each of the foreign atoms compensating each other in pairs, the quantity of said acceptor-forming elements and said donor-forming elements differing maximally

by 10%. The Auding patent describes the use of indium, boron, aluminium or zinc as the acceptor-forming dopant, and antimony or fluorine as the donor-forming dopant.

However, these films using stannic chloride have been found to be difficult to deposit in humid atmospheres and have been found to be unstable in the power densities of approximately 20 Watts per cm^2 required for rapid rise-time applications.

To the applicants' knowledge the films described in the Auding patent have not seen commercial use and are known only from this document.

SUMMARY OF THE INVENTION

The present applicants have found that a metal oxide layer of satisfactory stability in high power density applications may be obtained by doping with at least one and preferably two rare earth elements and that stability can be further enhanced by depositing the layer from different starting solutions than previously employed. The rare earth dopants are preferably cerium and lanthanum. Preferably these two rare earths are present in substantially equal concentrations. The presence of the rare earth dopants in the thin film layer has been found by the present applicants to have the effect of stabilising the oxidation state of the metal.

We have also found that stability at high temperatures may be obtained by further doping with equal quantities of donor and acceptor elements, and by avoiding the use of fluorine as a dopant. The preferred donor and acceptor elements for this purpose are respectively antimony and zinc.

In one aspect, the invention resides in a thin film electrical heating element including a layer of an electrically conducting metal oxide on an electrically insulating substrate, said metal oxide layer being doped with at least one rare earth element and being deposited on said substrate from an organometallic base solution.

Preferably the metal oxide is deposited on the substrate by pyrolysis of an organometallic base solution containing the at least one rare earth element.

In a preferred form the metal oxide layer is tin oxide and contains two rare earth elements such as cerium and lanthanum.

This aspect of the invention provides a thin film heating element which is capable of withstanding power densities of up to 10-20 Watts cm^{-2} and/or temperatures in excess of 600°C.

In another aspect, the invention resides in a method for the manufacture of a thin film heating element including the step of depositing a layer of metal oxide onto an electrically insulating substrate by pyrolysis of an organometallic base solution containing at least one rare earth element.

Preferably the base solution contains both cerium and lanthanum in concentrations up to 5 mol %.

We have found that superior results can be obtained if the film is prepared by spray pyrolysis from a solution of monobutyl tin trichloride. The stability of this material in high humidity enables consistent results to be obtained across varying atmospheric conditions, by reducing premature oxidation.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is graph showing the power dissipation versus time relationship for a thin film heating element made according to the invention.

Fig. 2 shows the relationship between temperature and power at steady state for five elements having power ratings between 500 and 1330 watts.

DESCRIPTION OF PREFERRED EMBODIMENTS

While some benefit will be obtained from quite low concentrations of the rare earth dopant, minimal effects will be observed with concentrations in the pyrolysis solution of 0.01 mol %, preferred concentrations of each of the cerium and lanthanum are between approximately 1.25 mol % and approximately 3.75 mol %. Preliminary tests have shown that stability of the metal oxide layer is maximised when substantially equal concentrations of two rare earth elements, such as cerium and lanthanum, are used. Generally speaking the concentration of these rare earths will be chosen as that which contributes to film stability at the power densities for which the film is intended. Best results for films intended for operation at 20 Watts cm^{-2} have been obtained using equal concentrations of approximately 2.5 mol %.

The film is preferably doped with substantially equal quantities of donor and acceptor elements, the preferred dopants being antimony and zinc. The concentrations of both antimony and zinc will be influenced by the resistivity which is required. We have found base solution concentrations for these materials in the region of 2.8 mol % to be suitable for heating element applications.

A useful characteristic of such films in their application as heating elements arises from the positive temperature coefficient resistance of the film. This enables elements to be produced which are self-regulating, in that they will initially operate at a higher wattage and, with increasing temperature, stabilise at the lower design wattage.

The substrate material will of course be chosen to suit the application. Suitable substrates include glass ceramics, silicon nitrides and other ceramic substrates as well as metallic substrates coated with high-temperature stable, electrically-insulating materials.

The preferred substrate temperatures for applying the base solution with dopants range from 500 to 750°C. Preferably, for application at 500°C, post annealing at approximately 600°C for at least one hour is carried out to assist in stabilising the film.

Films according to this invention were manufactured from a solution using the spray pyrolysis process. For this purpose, monobutyl tin trichloride was used as a base solution, with 2.8 mol % antimony chloride, 2.8 mol % zinc chloride, 2.5 mol % cerium and 2.5 mol % lanthanum.

These films were fabricated with effective resistances of 26 ohm, 30 ohm and 45 ohm to enable heaters of 2.2 kW, 1.8 kW and 1.2 kW respectively to be used, powered by a 240V mains supply voltage. The films were selectively deposited using high temperature masking inks which were removed by brushing after deposition of the film. The films deposited had a high degree of transparency. The resistive properties of the heating elements remained unchanged after 3500 cycles (40 minutes on and 20 minutes off) at 650°C.

As indicated above, the positive temperature coefficient of resistance of these elements enables a self-regulating characteristic to be obtained, with an initially high power dissipation which may be of advantage in achieving more rapid rise to operating temperature. Fig. 1 shows the typical behaviour of the elements, where power dissipation is plotted against time of operation. As will be observed, the dissipation of the element commences at a high level and decreases as the resistance of the element increases with temperature, until a steady state condition is achieved at the design power consumption. Upon temporary cooling of the element, for example through contact with a cooler body to be heated, power dissipation will temporarily increase, assisting in achieving rapid heating.

Fig. 2 shows the relationship between temperature and power at steady state for five elements having power ratings between 500 and 1330 watts.

Life tests have shown that the films are particularly stable on inert substrates like quartz 96% silica in temperatures up to 650°C with power densities in excess of $15.5W/cm^2$. The films on lower grades of glass ceramics having alkali impurities such as lithium and sodium were stable to 500°C at extremely high power densities.

Sheet resistances varying from around 60 ohms to above 400 ohms have been fabricated by varying the number of spray passes. The thin film thickness could be varied between 2000 Angstrom Units to around 14000 Angstrom Units by varying the number of spray passes. The films were deposited on various substrates including glass ceramics, alumina, silica glass and silicon nitride.

As well as their suitability in high temperature and/or high rise time applications, films made in accordance with the invention may be used in low temperature applications, such as comfort heating, refrigerating defrost, and general heating. Heating elements of tubular shape manufactured using the above technology can be used in heat exchangers for flow applications, air-conditioning re-heaters, hair dryers, washing and drying appliances, and can also be used as radiating surfaces.

While particular embodiments of this invention have been described, it will be evident to those skilled in the art that the present invention may be embodied in other specific forms without departing from the essential characteristics thereof. The present embodiments and examples are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

CLAIMS

1. A thin film electrical heating element including a layer of an electrically conducting metal oxide on an electrically insulating substrate, said metal oxide layer being doped with at least one rare earth element and being deposited on said substrate from an organometallic base solution.

2. A thin film heating element according to claim 1 wherein said metal oxide layer includes at least two rare earth elements.

3. A thin film heating element according to claim 2 wherein said two rare earth elements are present in said metal oxide layer in substantially equal concentrations.

4. A heating element according to claim 2 or 3 wherein said at least two rare earth elements include both cerium and lanthanum.

5. A heating element according to claim 1 wherein said metal oxide is tin oxide.

6. A heating element according to claim 2 wherein said metal oxide layer further includes substantially equal quantities of donor and acceptor elements.

7. A heating element according to claim 6 wherein said donor and acceptor elements are respectively antimony and zinc.

8. A heating element according to claim 6 wherein said metal oxide layer is substantially free of fluorine.

9. A heating element according to claim 1 wherein said heating element is stable at a power density of 20 watts cm^{-2}.

10. A heating element according to claim 1 wherein said heating element is stable at a temperature of 650°C.

11. A thin film heating element according to claim 1 wherein the or each rare earth element is present in said base solution at a concentration up to 5 mol %.

12. A thin film heating element according to claim 11 wherein said at least one rare earth element includes both cerium and lanthanum.

13. A thin film heating element according to claim 12 wherein cerium and lanthanum are each present in said base solution in the range of approximately 1.25 mol % to approximately 3.75 mol %.

14. A thin film heating element according to claim 13 wherein the concentration of each of cerium and lanthanum in said solution is approximately 2.5 mol %.

15. A thin film heating element according to claim 1 wherein said base solution further includes substantially equal quantities of donor and acceptor elements.

16. A thin film heating element according to claim 15 wherein each of said donor and acceptor elements are respectively antimony and zinc and are each present in said solution at a concentration of approximately 2.8 mol %.

17. A thin film heating element according to claim 1 or 12 wherein said base solution is monobutyl tin trichloride.

18. A thin film heating element according to Claim 1 wherein said metal oxide layer is deposited on said substrate from an organometallic base solution using a spray pyrolysis process.

19. A method for the manufacture of a thin film heating element including the step of depositing a layer of metal oxide onto an electrically insulating substrate by pyrolysis of an organometallic base solution containing at least one rare earth element.

20. A method according to claim 19 wherein said solution contains at least two rare earth elements.

21. A method according to claim 20 wherein said two rare earth elements are present in said solution in substantially equal concentrations.

22. A method according to claim 19 wherein said at least one rare earth element is present in said solution in the range of approximately 1.25 mol % to approximately 3.75 mol %.

23. A method according to claim 20 wherein said at least two rare earth element includes both cerium and lanthanum.

24. A method according to claim 23 wherein said cerium and lanthanum are each present in said solution in substantially equal concentrations.

25. A method according to claim 19 wherein said base solution is monobutyl tin trichlorde.

26. A method according to claim 19 wherein said solution further includes chlorides of at least one donor and at least one acceptor element, said donor chlorides and acceptor chlorides being present in said solution in substantially equal concentrations.

27. A method according to claim 26 wherein said donor chloride is antimony chloride and said acceptor chloride is zinc chloride.

28. A method according to claim 19 wherein said solution is substantially free of fluorine.

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Received 4 April 2000

29. A method according to claim 19 further including the step of annealing said metal oxide layer on said substrate for at least one hour at a temperature higher than the substrate temperature used during said pyrolysis.